

AMENDED SPECIFICATION

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PATENT SPECIFICATION



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Application Date (in United Kingdom): Jan. 13, 1943. No. 620/43.

Complete Specification Accepted: July 3, 1945.

COMPLETE SPECIFICATION

Improvements in or relating to the Emulsion Polymerisation and Copolymerisation of Methyl Alpha-Chloroacrylate

We, E. I. DU PONT DE NEMOURS AND Co., a corporation organised and existing under the laws of the State of Delaware, United States of America, located at 5 Wilmington, Delaware, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the

10 following statement:—

This invention relates to a new and improved process for the polymerisation of methyl alpha-chloroacrylate alone, or in admixture with at least one other 15 polymerisable mono-ethylenic compound.

Methyl alpha-chloroacrylate polymers possessing unusual hardness, clarity and high softening temperature can be obtained by the so-called bulk or casting 20 method of polymerisation. However, unmodified polymethyl alpha-chloroacrylate is deficient in flexibility and flow properties and is thus unsuited for certain applications where those properties are 25 essential. Although methyl alpha-chloroacrylate has been copolymerised with certain unsaturated compounds such as styrene with some improvement in flow and toughness, the degree of improvement 30 has remained insufficient for certain uses. Furthermore, methyl alpha-chloroacrylate has been copolymerised only with great difficulty or not at all with certain unsaturated polymerisable compounds.

35 This invention has as its object to provide a new and improved method for the polymerisation of methyl alpha-chloroacrylate. Another object is to provide a new and improved method for 40 the conjoint polymerisation of methyl alpha-chloroacrylate with at least one other polymerisable compound containing

a single ethylenic linkage. Another object is to provide a method for obtaining relatively tougher and more elastic 45 copolymers of methyl alpha-chloroacrylate with other polymerisable compounds without serious sacrifice of the softening temperatures of such copolymers. Other objects will be apparent from the following 50 description of the invention.

These objects are accomplished according to the present invention by a process which comprises emulsifying methyl alpha-chloroacrylate alone, or in admixture with one or more other polymerisable 55 compounds containing a single ethylenic linkage, in an aqueous medium containing a dissolved salt of perdisulphuric acid and an acid-stable, as hereinafter defined, dispersing agent comprising a long-chain acyclic hydrocarbon substituted with one and only one nitrogen-free, anionic solubilising radical, said radical being either $-\text{SO}_2\text{OX}$ or $-\text{OSO}_2\text{OX}$, 60 where X is an alkali metal, and then polymerising the polymerisable compound or compounds while in emulsion at a temperature between the freezing point of the aqueous phase and 80° C. 70

It is preferred to carry out the polymerisation whilst the emulsion is in a closed vessel containing a substantially oxygen-free gas space.

The term "acid-stable" as used herein 75 refers to agents whose activity is unaffected in media of mild acidity e.g. pH 3 to 5, and excludes soaps which are decomposed under these conditions to form free fatty acids and inorganic salts. 80

The term "long-chain acyclic hydrocarbon" is used herein with reference to acyclic hydrocarbons having a chain of 12-18 carbon atoms.

[Price 1/-]

Price 4s 6d.

The exact manner of practising this invention will vary depending upon the particular compounds processed; however, the following will illustrate its application. An aqueous medium containing about 0.1 to 2% of a perdisulphate salt and about 1 to 5% of a dispersing agent as defined above is placed in a suitable pressure vessel which is provided with a means of agitation such as stirring or shaking. This is followed by the addition of a mixture of methyl alpha-chloroacrylate and at least one other polymerisable monoethylenic compound. The air in the free space of the vessel is displaced by an inert gas such as nitrogen and the vessel is then sealed. It is thereafter heated at a constant temperature in the range of 30° to 50° C. with constant or intermittent agitation until polymerisation has proceeded to the desired extent.

Our invention is illustrated but in no way limited by the following examples in which all parts given are by weight.

EXAMPLE I

60/40 METHYL ALPHA-
CHLOROACRYLATE/METHYL ACRYLATE
COPOLYMER

A solution of 7.8 parts of a commercial dispersing agent containing about 22% of sodium cetyl sulphate as active ingredient in 111 parts of water is prepared by heating the mixture on a steam bath. The solution is placed in a suitable pressure vessel, cooled to room temperature and 36 parts of methyl alpha-chloroacrylate, 24 parts of methyl acrylate and 0.612 part of ammonium perdisulphate added in the order named. The air in the bottle is replaced with nitrogen after which the contents of the reaction vessel are agitated at 45° C. for 24 hours. The mixture is diluted with an equal volume of water and steamed to remove residual monomers. The emulsion is coagulated with 10% aluminium sulphate solution (20 parts) and the product filtered, thoroughly washed with water, and dried. The yield of copolymer is 57.8 parts or 96.3% of theory. A specimen of this product moulded at 165° C. and 2000 lbs./sq. in. pressure is unusually tough. The softening temperature of the product is 83° C.

EXAMPLE II

60/40 METHYL ALPHA-
CHLOROACRYLATE/METHYL ACRYLATE
COPOLYMER

To a solution of 12 parts of a commercial dispersing agent containing about 32% of the sodium salt of sulphonated paraffin oil in 111 parts of water is added 36 parts of methyl alpha-chloroacrylate, 24 parts of methyl acrylate, and 0.6 part of ammonium perdisulphate in the order named. The mixture is placed in a

suitable pressure vessel, which is flushed with nitrogen to remove air, sealed, and agitated slowly by a mechanical rocker for 24 hours at 45° C. The resulting dispersion is diluted with an equal volume of water, steam is passed into the mixture to remove residual monomers, and the dispersed copolymer is coagulated by adding 20 parts of a 10% solution of aluminium sulphate. The product is filtered, thoroughly washed with water, and dried. The yield is 57.5 parts or 95.8% of theory. Extremely tough shaped products are obtained by moulding for 6 minutes at 165° C. under 2000 lbs./sq. in. pressure. The softening temperature of the product is 82.5° C.

EXAMPLE III

50/50 METHYL ALPHA-
CHLOROACRYLATE/METHYL ACRYLATE
COPOLYMER

A solution of 7.8 parts of a commercial sodium cetyl sulphate dispersing agent containing about 22% active ingredients, in 111 parts of water, is prepared by heating the mixture on a steam bath. The solution is placed in a suitable pressure vessel, cooled to room temperature and 30 parts of methyl alpha-chloroacrylate, 30 parts of methyl acrylate, and 0.6 part of ammonium perdisulphate added in the order named. The air in the vessel is replaced by nitrogen after which the contents are agitated at 45° C. for 24 hours. The dispersion obtained is diluted with an equal volume of water after which steam is passed into the mixture to remove residual monomers. The emulsion is coagulated with 10% aluminium sulphate solution (20 parts) and the product filtered, thoroughly washed with water, and dried. The yield is 58.8 parts or 98% of theory. A specimen of this product moulded at 165° C. and 2000 lbs./sq. in. pressure is unusually tough. The softening temperature of the product is 86.5° C. Pressed films of the product are extremely tough, can be bent double repeatedly without breaking, and are capable of standing very severe treatment.

EXAMPLE IV

55/45 METHYL ALPHA-
CHLOROACRYLATE/METHYL ACRYLATE
COPOLYMER

A solution of 7.8 parts of commercial sodium cetyl sulphate dispersing agent containing about 22% active ingredients in 111 parts of water is prepared by heating the mixture on a steam bath. The solution is placed in a suitable pressure vessel, cooled to room temperature and 33 parts of methyl alpha-chloroacrylate, 27 parts of methyl acrylate, and 0.6 part of ammonium perdisulphate added in the order named. The air in the

vessel is replaced with nitrogen after which the reaction mixture is agitated at 45° C. for 22 hours. The resulting milky dispersion is diluted with an equal volume of water and steamed to remove residual monomers. The emulsion is coagulated with 10% aluminium sulphate solution (20 parts) and the product filtered, thoroughly washed with water, and dried. The yield is 58.7 parts or 97.8% of theory. A specimen of this product moulded at 165° C. and 2000 lbs./sq. in. pressure is unusually tough. Pressed films of the product can be bent double repeatedly and subjected to other severe treatment without cracking. The softening temperature of the product is 85.5° C.

EXAMPLE V

70/30 METHYL ALPHA-
20 CHLOROACRYLATE/METHYL ACRYLATE
COPOLYMER

Seven and eight-tenths parts of sodium cetyl sulphate dispersing agent containing about 22% active ingredient is dissolved in 111 parts of water by heating the mixture on a steam bath. The solution is placed in a suitable pressure vessel, cooled to room temperature and 42 parts of methyl alpha-chloroacrylate, 18 parts of methyl acrylate, and 0.6 part of ammonium perdisulphate added in the order named. The air in the vessel is replaced with nitrogen after which the reaction mixture is agitated at 40° C. for 22 hours. The product is diluted with an equal volume of water and steamed to remove unreacted monomers. The dispersion is then coagulated with 10% aqueous aluminium sulphate solution (20 parts), the product filtered, thoroughly washed with water, and dried. The yield is 59.5 parts or 99.2% of theory. This product has good moulding properties and strength but is not as tough as the product of Example IV.

EXAMPLE VI

80/20 METHYL ALPHA-
CHLOROACRYLATE/METHYL ACRYLATE
COPOLYMER

50 One hundred eighteen and eight-tenths parts of sodium cetyl sulphate dispersing agent solution is made up as described in Example V and charged into a suitable pressure vessel. The solution is cooled to room temperature and 48 parts of methyl alpha-chloroacrylate, 12 parts of methyl acrylate, and 0.6 part of ammonium perdisulphate added in the order named. The air in the vessel is replaced with nitrogen after which the monomer emulsion is agitated at 40° C. for 22 hours. The dispersion is then removed to a separate vessel, diluted with an equal volume of water, after which steam is passed into the mixture to remove resi-

dual monomers. The emulsion is coagulated with 10% aluminium sulphate solution (20 parts) and the product filtered, thoroughly washed with water, and dried. The yield is 59.7 parts or 99.5% of theory. The product moulds readily at 150° C. and 2000 lbs./sq. in. pressure to give articles of good strength. However, due to the reduced amount of methyl acrylate in the copolymer, the products are not nearly as tough as the product described in Example IV.

EXAMPLE VII

50/50 METHYL ALPHA-
CHLOROACRYLATE/BUTYL METHACRYLATE 80
COPOLYMER

A solution of 7.8 parts of commercial sodium cetyl sulphate dispersing agent containing about 22% active ingredients, in 111 parts of water, is prepared by heating the mixture on a steam bath. The solution is placed in a suitable pressure vessel, cooled to room temperature, and 30 parts of methyl alpha-chloroacrylate, 30 parts of butyl methacrylate, and 0.6 part of ammonium perdisulphate added in the order named. The air in the bottle is replaced with nitrogen after which the contents of the reaction vessel are agitated at 45° C. for 24 hours. The mixture is diluted with an equal volume of water after which steam is passed into the mixture to remove residual monomers. The emulsion is coagulated with 10% aluminium sulphate solution (20 parts) and the product is filtered, thoroughly washed with water, and dried. The yield is 58.4 parts or 97.3% of theory. A specimen of this product moulded at 160° C. and 2000 lbs./sq. in. pressure is unusually tough. The softening temperature of the product is 70° C.

EXAMPLE VIII

60/40 METHYL ALPHA-
CHLOROACRYLATE/BUTYL METHACRYLATE 110
COPOLYMER

A solution of 7.8 parts of commercial sodium cetyl sulphate dispersing agent containing about 22% active ingredients, in 111 parts of water is prepared by heating the mixture on a steam bath. The solution is placed in a suitable pressure vessel, cooled to room temperature, and 36 parts of methyl alpha-chloroacrylate, 24 parts of butyl methacrylate, and 0.6 part of ammonium perdisulphate added in the order named. The air in the bottle is replaced with nitrogen after which the contents of the reaction vessel are agitated at 45° C. for 24 hours. The mixture is diluted with an equal volume of water after which steam is passed into the mixture to remove residual monomers. The emulsion is coagulated with 10% aluminium sulphate solution (20 parts), the

product filtered, thoroughly washed with water, and dried. The yield is 58.8 parts or 98% of theory. A specimen of this product moulded at 165° C. and 2000 5 lbs./sq. in. pressure is very tough. The softening temperature of the product is 78° C.

EXAMPLE IX

70/30 METHYL ALPHA-

10 CHLOROACRYLATE/BUTYL METHACRYLATE COPOLYMER

A solution of 7.8 parts of commercial sodium cetyl sulphate dispersing agent containing about 22% active ingredients, 15 in 111 parts of water is prepared by heating the mixture on a steam bath. The solution is placed in a suitable pressure vessel, cooled to room temperature and 42 parts of methyl alpha-chloroacrylate, 18 20 parts of butyl methacrylate, and 0.6 part of ammonium perdisulphate added in the order named. The air in the bottle is replaced with nitrogen after which the contents of the reaction vessel are agitated 25 at 40° for 22 hours. The mixture is diluted with an equal volume of water after which steam is passed into the mixture to remove residual monomers. The emulsion is coagulated with 10% aluminium sulphate solution (20 parts), and the 30 product filtered, thoroughly washed with water, and dried. The yield is 59.8 parts or 99.7% of theory. The product upon moulding at 145° C. and 2000 lbs./sq. in. 35 pressure gives pale yellow, transparent, strong specimens which, however, are not as tough as the products described in Example VIII.

EXAMPLE X

80/20 METHYL ALPHA-

CHLOROACRYLATE/BUTYL METHACRYLATE COPOLYMER

A solution of 7.8 parts of commercial sodium cetyl sulphate dispersing agent 45 containing about 22% active ingredients, in 111 parts of water is prepared by heating the mixture on a steam bath. The solution is placed in a suitable pressure vessel, cooled to room temperature and 48 50 parts of methyl alpha-chloroacrylate, 12 parts of butyl methacrylate, and 0.6 part of ammonium perdisulphate added in the order named. The air in the bottle is replaced with nitrogen after which the 55 contents of the reaction vessel are agitated at 40° C. for 22 hours. The mixture is diluted with an equal volume of water after which steam is passed into the mixture to remove residual monomers. 60 The emulsion is coagulated with 10% aluminium sulphate solution (20 parts), the product filtered, thoroughly washed with water, and dried. The yield is 59.8 parts or 99.7% of theory. The product 65 moulds well at 145° C. and 2000 lbs./sq.

in. pressure to give transparent, strong moulded specimens which, however, are not as tough as the products described in Examples VII and VIII.

EXAMPLE XI

60/40 METHYL ALPHA-

CHLOROACRYLATE/VINYL ACETATE COPOLYMER

A solution of 7.8 parts of commercial sodium cetyl sulphate dispersing agent 75 containing about 22% active ingredients, in 111 parts of water is prepared by heating the mixture on a steam bath. The solution is placed in a suitable pressure vessel, cooled to room temperature and 80 36 parts of methyl alpha-chloroacrylate, 24 parts of vinyl acetate and 0.6 part of ammonium perdisulphate added in the order named. The air in the bottle is replaced with nitrogen after 85 which the contents of the reaction vessel are agitated at 45° for 24 hours. The mixture is diluted with an equal volume of water after which steam is passed into the mixture to remove residual monomers. 90 The emulsion is coagulated with 10% aluminium sulphate solution (20 parts) and the product filtered, thoroughly washed with water, and dried. The yield is 49.6 parts or 82.7% of theory. 95

EXAMPLE XII

80/20 METHYL ALPHA-

CHLOROACRYLATE/DIETHYL ITACONATE COPOLYMER

A solution of 7.8 parts of commercial sodium cetyl sulphate dispersing agent 100 containing about 22% active ingredients in 111 parts of water is prepared by heating the mixture on a steam bath. The solution is placed in a suitable pressure vessel, 105 cooled to room temperature, and 48 parts of methyl alpha-chloroacrylate, 12 parts of diethyl itaconate, and 0.6 part of ammonium perdisulphate added in the order named. The air in the bottle is 110 replaced with nitrogen after which the contents of the reaction vessel are agitated at 25° C. for 67 hours. The mixture is diluted with an equal volume of water after which steam is passed into the 115 mixture to remove residual monomers. The emulsion is coagulated with 10% aluminium sulphate solution (20 parts), the product filtered, thoroughly washed with water and dried. The yield is 58 120 parts or 96.6% of theory. This product has good flow and moulds readily at 150° C. and 2000 lbs./sq. in. pressure.

EXAMPLE XIII

70/30 METHYL ALPHA-

CHLOROACRYLATE/FURYLETHYLENE COPOLYMER

A solution of 7.8 parts of commercial sodium cetyl sulphate dispersing agent 125 containing about 22% active ingredients, 130

in III parts of water prepared by heating the mixture on a steam bath. The solution is placed in a suitable pressure vessel, cooled to room temperature and 5 42 parts of methyl alpha-chloroacrylate, 18 parts of furylethylene and 0.6 parts of ammonium perdisulphate added in the order named. The air in the bottle is replaced with nitrogen after which the 10 contents of the reaction vessel are agitated at 45° C. for 22 hours. The mixture is diluted with an equal volume of water after which steam is passed into the mixture to remove residual monomers. 15 The emulsion is coagulated with 10% aluminium sulphate solution (20 parts) and the product filtered, thoroughly washed with water, and dried. The yield is 51.3 parts or 85.5% of theory. The 20 product moulds readily at 145° C. and 2000 lbs./sq. in. pressure.

EXAMPLE XIV
METHYL ALPHA-CHLOROACRYLATE
POLYMER

25 A solution of 7.8 parts of commercial sodium cetyl sulphate containing about 22% active ingredient, in 111 parts of water is prepared by warming on the steam bath. The solution is cooled to 30 room temperature and 60 parts of methyl alpha-chloroacrylate and 0.612 part of ammonium perdisulphate added. The air in the polymerisation vessel is flushed out with nitrogen and the mixture agitated. 35 Polymerisation begins almost at once and is complete in 15 hours at room temperature (25° C.). Steam is passed into the mixture after which it is cooled to 50° C. and 20 parts of 10% aluminium sulphate 40 solution added with stirring to coagulate the dispersion. The product which separates is filtered, thoroughly washed with water and dried. The yield amounts to 54 parts or 94% of theory. The 45 polymer moulds readily at 160° and 2000 lbs./sq. in. pressure to give transparent specimens.

It should be pointed out that the use 50 with one or more of the dispersing agents defined herein as illustrated in the foregoing examples brings about results that are both unique and superior to those obtained with any other catalyst-dispersing agent combination hitherto disclosed. The relative rapidity with 55 which polymerisation takes place even at moderately low temperatures is unexpected. It should be further pointed out 60 that copolymers prepared using this invention are desirably higher in molecular weight than those produced using emulsion processes hitherto disclosed. An uniquely effective means for 65 obtaining copolymers of methyl alpha-

chloroacrylate with, for example, the following substances is thus provided: Methyl acrylate, ethyl acrylate, butyl acrylate, octyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, octyl methacrylate, 2-nitro-2-methyl propyl methacrylate, methoxyethyl methacrylate, chloroethyl methacrylate, phenyl methacrylate, cyclohexyl methacrylate, acrylamide and methacryl amide or mono-alkyl substitution products thereof; unsaturated ketones such as methyl vinyl ketone, phenyl vinyl ketone, and methyl isopropenyl ketone; vinyl carboxylates such as vinyl acetate, vinyl 80 propionate and vinyl stearate. With regard to proportions, this invention is chiefly concerned with mixtures of methyl alpha-chloroacrylate and one other operable monomer which contain from about 85 5 to about 95 per cent. of methyl alpha-chloroacrylate by weight. It is apparent that the properties of the copolymers will depend to a great extent on the type and amount of the other ingredients to be 90 copolymerised with methyl alpha-chloroacrylate. It is within the scope of the invention to polymerise methyl alpha-chloroacrylate conjointly with two or more monoethylenic compounds polymer- 95 isable under the same conditions.

The polymerisation catalysts used in this invention include the water-soluble salts of perdisulphuric acid. In addition to the ammonium salt disclosed in the 100 examples, there may also be used the sodium, potassium, lithium, barium, magnesium and calcium perdisulphates. It is known that the sulphate ion appears 105 in aqueous solutions of perdisulphates. For this reason, while the water-soluble alkaline earth metal salts are operable, they are not usually employed because of their tendency to form a precipitate of 110 the corresponding alkaline earth sulphate. The preferred salts are the ammonium and alkali metal salts. Ammonium perdisulphate is especially suitable for economic considerations.

The concentration of perdisulphate salt 115 employed may be varied within wide limits. For instance, amounts of perdisulphates varying from 0.1% to 10% of the quantity of monomer employed are operable. With respect to economy of 120 catalyst, quality of product, and rapidity of polymerisation, the preferred proportion of perdisulphate salt lies in the range of 0.1 to 4% based on the total weight of monomers employed.

As operable dispersing agents in addition to those disclosed in the foregoing examples, there may be mentioned the alkali metal salts of the following long chain alkyl acid sulphates and acid 130

sulphonates: Dodecyl-1 acid sulphate, tetradecyl-1 acid sulphate, octadecyl-1 acid sulphate, oleyl-1 acid sulphate, dodecane-1-sulphonic acid, tetradecane-1-sulphonic acid, hexadecane-1-sulphonic acid and octadecane-1-sulphonic acid. The salts of long chain sulphonated paraffin oil hydrocarbons are especially effective dispersants and need be employed only in small proportions to achieve the desired results. It will be understood that the dispersants to which reference is made above are commercial materials which, because of the methods used in their manufacture and because of the sources of the starting materials, are usually not produced in a high state of purity and may contain minor constituents which influence the effectiveness of the active ingredient. Polymerisation systems of the present invention may also contain inorganic salts, long chain primary alcohols, carbohydrate derivatives, and polyvinyl alcohol.

Using the rate of polymerisation as a criterion, the invention contemplates the use of dispersing agent active ingredients in concentrations of 0.2 to 5% based on the weight of the aqueous medium in which the polymerisation is brought about. Within this range, the preferred concentration will in general depend upon the proportion of monomer present, but is usually from 0.5 to 4%. From the stand-point of economy and to facilitate removing the dispersing agent from the polymerised product, it is customary to use approximately the smallest amount of dispersing agent which promotes polymerisation at the desired rate. It is to be understood that when reference is made to the use of definite percentages of dispersing agents, these values are calculated on the basis of the known active ingredient concentration in the commercial dispersants.

It may also be pointed out that the effectiveness of the dispersing agent, especially if small concentrations are employed, is enhanced by agitation of the mixture. Any method of agitation may be used in producing and maintaining the emulsion. The most commonly employed method of mixing is stirring, preferably in vessels containing suitable baffles. Other methods included shaking, tumbling and the use of turbomixers. The dispersing agents operable in this invention are in general useful in forming stable emulsions, which after they are once formed, require little or no agitation thereafter. It has been found, however, that polymerisation occurs more rapidly in certain emulsions while they are being agitated. It is accordingly pre-

ferred to assist the dispersing agent in producing and maintaining the emulsion by mechanical means, which may or may not be continuous.

The process of this invention may be carried out in alkaline, acid or neutral media. However, since the process involves materials susceptible to hydrolysis, care must be taken to operate in media with pH values at which the tendency to hydrolyse is at a minimum. It is, therefore, beneficial to employ aqueous media having initial pH values of about 1.5 to 5 in the copolymerisation process. If it is desired to avoid changes in pH during the course of the polymerisation, suitable buffers may be added to the aqueous medium.

The operability of the invention is not confined to any particular proportion of polymerisable monomer or monomers relative to the amount of aqueous media present. Thus, the ratio of the aqueous to the non-aqueous phase may vary between approximately 10:1 and 1:1 by weight. In general, it is preferred to employ aqueous/non-aqueous ratios between approximately 4:1 and 1:1 by weight, since for a given reaction vessel the time-space yield is greatly reduced by the use of higher ratios. It can further be said that higher aqueous/non-aqueous ratios generally tend to favour the production of lower molecular weight products. It is also helpful in maintaining an emulsion if the proportion by weight of non-aqueous to aqueous phases is not greater than 1:1.

As is well known, the dependence of the rate of vinyl polymerisation upon the temperature is very important, and low temperatures have not been generally used because the corresponding rate of reaction is impractically low. The present invention is operated at temperatures above the freezing point of the aqueous phase which is somewhat below 0°C. up to 80°C., above which the starting materials and product may be adversely affected by the aqueous medium. It is preferred to employ temperatures in the range of 20°C. to 60°C.

It is realised that the presence of oxygen in the polymerisation vessel, while not appearing to have a deleterious effect on the properties of the polymers of this invention, may retard the rate of polymerisation in certain cases. In these cases, it is therefore preferable to displace the air from the polymerisation vessel by means of a gas which does not reduce the rate of polymerisation. Suitable gases are nitrogen, carbon dioxide, methane and helium. These gases may be passed through the free space of the polymerisa-

tion vessel until the air has been completely displaced or may be introduced under sufficiently high pressure that the oxygen originally present is so greatly 5 diluted as to have little effect on the rate of polymerisation.

The process is not limited to any particular apparatus, but it is important that the reaction vessel shall be constructed 10 of material which has no effect on the rate of polymerisation or on the quality of the products and is not affected by the aqueous medium used in carrying out the polymerisation. Suitable vessels may be 15 constructed of stainless steel, nickel, silver, or lead. Vessels equipped with glass or enamel liners may also be used.

At the conclusion of polymerisation, the products of this invention may be 20 isolated as finely divided powders by a variety of methods. For example, the dispersion may be sprayed into a heated and/or evacuated chamber whereby the water is removed as vapour and the 25 polymer falls to the bottom of the chamber. The polymer may also be isolated by cooling the dispersion below the freezing point of the aqueous medium or by the addition of a large volume of a 30 lower aliphatic alcohol such as methanol or ethanol. The most satisfactory method consists in adding an appropriate amount of an electrolyte solution to the diluted aqueous dispersion with rapid agitation at 35 a temperature just below the point at which the precipitated particles tend to cohere. This procedure yields a polymer in the form of dense granular particles which are readily filtered and washed. 40 Suitable electrolytes include sodium chloride, sodium sulphate, hydrochloric acid, phosphoric acid, calcium chloride, magnesium sulphate, lead nitrate, lead acetate, stannous chloride, and aluminium 45 sulphate. After precipitation of the polymer it is filtered and washed repeatedly with water to remove traces of electrolyte and dispersing agent which may adhere to the particles. The polymers 50 are conveniently dried in ovens at moderate temperatures or in open trays under a gentle stream of warm dust-free air.

The products prepared according to the 55 present invention may be used for the preparation of plastics, coatings, films, foils, fibres, and adhesives. For any of these purposes, the polymer may be combined with or prepared in the presence of 60 plasticisers, stabilisers, fillers, pigments, dyes, softeners, natural resins or other synthetic resins.

When the products are used as coating or impregnating agents for porous 65 materials, it is possible to apply the

emulsions directly to the material to be coated without the intermediate isolation of the polymer.

Our copending application No. 1120/43 (Serial No. 570,330) describes a process 70 for the production of polymeric materials which comprises subjecting to polymerising conditions an aqueous emulsion of vinyl chloride, in the presence or absence of other ethylenic compounds, said emul- 75 sion containing a dissolved salt of perdisulphuric acid and an acid-stable dispersing agent of the type herein described.

We are aware that British Patent 80 570,711 to Imperial Chemical Industries Ltd. claims, *inter alia*, a process which comprises polymerising an emulsion of a mixture of an asymmetrical dihalogenated ethylene and one or more polymerisable compounds containing the group $\text{CH}_2=\text{C}<$, for example methyl alpha-chloroacrylate, in an aqueous medium containing a dissolved salt of perdisulphuric acid and a dispersing 90 agent consisting of an alkali metal salt of a long chain alkyl acid sulphate or acid sulphonate containing 12 to 18 carbon atoms whose activity is unaffected at pH values between 3 and 5. We make 95 no claim to any subject matter claimed in British Patent 570,711.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to 100 be performed, we declare that, subject to the above disclaimer, what we claim is:—

1. A process for the production of polymeric materials which comprises emulsifying methyl alpha-chloroacrylate 105 in the absence of other polymerisable compounds in an aqueous medium containing a dissolved salt of perdisulphuric acid and an acid-stable, as hereinbefore defined, dispersing agent comprising a 110 long chain acyclic hydrocarbon substituted with one and only one nitrogen-free anionic solubilising radical, said radical being either $-\text{SO}_2\text{OX}$ or $-\text{OSO}_2\text{OX}$, where X is an alkali metal, and then 115 polymerising said polymerisable compound while in emulsion at a temperature between the freezing point of the emulsion and 80°C .

2. A process for the production of 120 polymeric materials which comprises emulsifying methyl alpha-chloroacrylate in admixture with one or more other polymerisable compounds containing a single ethylenic linkage in an aqueous 125 medium containing a dissolved salt of perdisulphuric acid and an acid-stable, as hereinbefore defined, dispersing agent comprising a long chain acyclic hydrocarbon substituted with one and only one 130

nitrogen-free anionic solubilising radical, said radical being either $-\text{SO}_2\text{OX}$ or $-\text{OSO}_2\text{OX}$, where X is an alkali metal, and then polymerising said polymerisable compounds while in said emulsion at a temperature between the freezing point of the emulsion and 80°C .

3. A process as claimed in Claim 2 in which at least one of the other polymerisable compounds is an ester of an alpha methylene aliphatic monocarboxylic acid.

4. A process as claimed in Claim 2 in which at least one of the other polymerisable compounds is a vinyl carboxylate.

5. A process as claimed in Claim 2 in which at least one of the other polymerisable compounds is methyl acrylate.

6. A process as claimed in Claim 2 in which at least one of the other polymerisable compounds is butyl methacrylate.

7. A process as claimed in either of Claims 5 and 6 in which the mixture of polymerisable compounds contains from 50 to 60% of methyl alpha-chloroacrylate.

8. A process according to any of the preceding claims in which the polymerisation is carried out at a temperature between 20°C . and 60°C .

9. A process according to any of the preceding claims in which the dissolved salt of perdisulphuric acid is selected from the group consisting of the alkali metal and ammonium salts.

10. A process according to any of the preceding claims in which the dispersing agent is sodium cetyl sulphate.

11. A process as claimed in any of the preceding claims 1-9 in which the dispersing agent is the sodium salt of sulphonated paraffin oil.

12. A process as claimed in any of the preceding claims in which the polymerisation is carried out in a substantially oxygen-free atmosphere over said emulsion.

13. A process for the production of polymeric materials substantially as hereinbefore described with reference to each of the foregoing examples.

14. Polymeric materials whenever produced by a process claimed in any of the preceding claims.

Dated this 13th day of January, 1943.

E. A. BINGEN,
Solicitor for the Applicants.

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